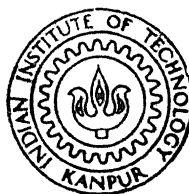


Electrophoretic Deposition of Titanium Dioxide From Aqueous Suspensions

**By
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**DEPARTMENT OF METALLURGICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
MARCH, 1976**

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Electrophoretic Deposition of Titanium Dioxide From Aqueous Suspensions

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY

By
RANJIT KUMAR DAS

to the
**DEPARTMENT OF METALLURGICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
MARCH, 1976**



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CERTIFICATE

Certified that this work on ' Electrophoretic deposition of Titanium dioxide from aqueous suspensions ' has been carried out under our supervision and that it has not been submitted elsewhere for a degree.



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RKDAS
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ABSTRACT

Investigations have been carried out to determine conditions suitable for electrophoretic deposition of titanium dioxide powder from aqueous suspensions. The effect of a number of variables such as voltage, pH, amount of solids, additives, etc., has been studied. It has been observed that the quality of water plays an important role in the deposition process. Water of low conductivity gives better deposits. Conditions desirable for a deposit of good quality are given.

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CHAPTER I

INTRODUCTION

Electrophoresis -

Electrophoresis is the phenomenon associated with the movement of colloidal particles, suspended in aqueous or non- aqueous media in an electrical field. In recent years this phenomenon has found wide application in the paint, rubber and plastic industries, field of medicine, automobile industry, etc.

Although the phenomenon of electrophoresis has been observed and investigated for almost 100 years, only very limited use has been made of electrophoresis as a method of applying coatings to materials. The early investigations were mainly concerned with producing layers to fill a cavity or a mould, but rarely to produce a coherent⁽¹⁾ deposit. It is interesting to note that metal oxide deposition by electrophoresis was apparently achieved as early as 1927⁽²⁾. However similar work was not continued.

The interesting metallurgical applications of electrophoresis have been revived in recent years. It is now recognised that the technique provides an efficient method of depositing metals, alloys and ceramic materials. Electrophoretic coatings have been developed for resistance to oxidation, corrosion, and for producing surfaces with desirable properties. The filaments of vacuum tube are

electrophoretically coated with Barium - Strontium carbonate, which are subsequently oxidized on heating (3) Nickel oxide and chromium oxide has been co-deposited and reduced by H_2 to produce a stainless steel coating (4)

Carbides and silicides can be deposited with reducible metallic oxide to form ceramic coating Alternately some oxide coatings may be carburized Electrophoretic deposition may also be used as a ceramic fabrication technique

A large number of parameters influence the phenomenon of electrophoresis These include the physico-chemical nature of the particles being deposited, the nature of the medium, pH, temperature, voltage, current, etc Consequently, detailed experiments need to be undertaken to ascertain the optimum deposition conditions

Both aqueous and non-aqueous solutions have been used as the medium for electrophoretic deposition Since the dielectric constants of the organic solvents are low, voltages as large as 2000 volts are often needed for deposition However they have been used more frequently than aqueous medium Organic solutions have been used as the media since they have higher densities which reduce the settling rate of suspension, good chemical stability, low electrical conductivity which

minimizes IR losses, etc

High voltages required for electrophoretic deposition presents fire hazards. Again, many organic solvents are toxic reagents and are therefore health hazards requiring special handling. They are often expensive. Aqueous solutions are generally expected to be free of the aforesaid disadvantages of organic solutions. Accordingly, some recent investigations have been directed at deposition from aqueous suspension (4,5)

The aim of the present investigation is to obtain the optimum conditions for deposition of oxide powders from aqueous solution. Titanium dioxide was chosen as a model system. The investigation aims at studying the effect of many important parameters namely, voltage, time, pH, concentration of the suspension, organic additives, etc

CHAPTER II

LITERATURE REVIEW AND THEORETICAL BACKGROUND

Literature Review -

It has been mentioned in chapter-I that although the phenomenon of electrophoretic deposition was discovered a century ago its exploitation in laboratory investigation or commercial application has been slow and sporadic. For example although a technique for coating the inside surface of tin cans by wax was described in the literature⁽¹⁾, the technique was neither persuaded in the laboratory nor applied commercially. Moreover, most of the early investigations were non-metallurgical in nature. Some of the pioneering investigations, which are of direct relevance to metallurgists, are briefly reviewed in this chapter.

Deposits from Organic solutions -

Fahnoe and coworkers⁽⁶⁾ deposited aluminium oxide and nickel oxide particles of very fine size (325 mesh) from thick paste in isopropyl alcohol, with a direct current under 100 V applied for 10 seconds.

The suspension produced a cathodic coating approximately 0.4×10^{-4} inch thick, with an electrode spacing of ~~1~~ 2 inch. After the appropriate post treatments the coating was useful as metal bonded abrasive surfaces for precision laps and dies.

Benjamin and Osborn⁽⁷⁾ investigated the deposition of carbonates of barium-strontium (0.5-50 particle diameter) using nitrocellulose binder and acetone as the suspending vehicle. Small quantities of ethylene glycol were added to reduce particle settling and solvent evaporation. These investigations did not report other deposition conditions.

Senderof and Junior⁽⁸⁾ have deposited dense barium titanate on metal sheets. The appropriate amounts of BaTiO_3 , diethyl glycol, dimethyl ether, and organic substance called Kenetrol 60 were mixed and ball-milled for about 18 hours. The additional amounts of the dimethyl compounds were added and milling continued for another two hours. The resultant colloidal dispersion was used for electrophoretic deposition with a metal screen cathode and a metal sheet anode. Deposits approximately 0.003 inch thick were obtained on the anode in about one minute using voltages between 500 to 2000 V.

Werner and Rade Jr.⁽⁹⁾ deposited alloy containing 80% nickel and 20% chromium using a suspension of metal and oxide powders in isopropyl alcohol, nitromethane, and zein solutions. Coatings of 2 to 3×10^{-4} inch

thickness were deposited on the cathode in 30 to 60 seconds at 20 V. After the deposition the coatings were densified and sintered to produce a dense structure with oxidation resistant properties.

Coatings of a number of elements (B, Zr, Au, Nb, Mo etc.) have been deposited ⁽¹⁰⁾, using metal powders in the size range 1 to 20 μ , with optimum size of 6 microns. It was found that the deposition rate increases with voltage up to about 700 V and then decreases at higher voltages. High voltages were necessary because the suspending media was organic, namely a mixture of isopropyl alcohol and methane.

Several other investigations have been aimed at deposition from organic baths which have been reviewed by Fisch ⁽¹¹⁾.

Deposits from Aqueous solutions -

Only a limited number of studies on deposition from aqueous solutions have been reported in the literature. Some of the recent investigations are done by Fisch ⁽¹¹⁾, Caley and Flengas ⁵, and Kucharski ⁽¹²⁾.

Fisch has developed, on a laboratory scale, a process for electrophoretic deposition of metals from aqueous suspension formed by mixing metal powder with an amine stabilized acrylic resin, glycerol, and a detergent wetting agent in

de-ionized (D I) water It should be noted that electrophoretic deposition is more difficult in ordinary distilled water because of high conductivity For suspension in D I water the conductivity is mainly due to electrophoretic mobility of the particles rather than mobility of ions

In the work reported by Fisch⁽⁴⁾, aluminate coatings were obtained from aqueous suspension using an amine stabilized resin as dispersant in distilled water, the pH of the bath was 7.8 to 8.3 and the flake particle size was 7.5 μ or less Subsequently Caley and Flengas⁽⁵⁾ have investigated electrophoretic transport for the suspension of oxides NiO, Cr_2O_3 , Fe_2O_3 , MnO, and TiO_2 in aqueous colloidal suspension Electrophoretic mobilities, zeta potential, electrical conductivities, viscosities and optimum plating conditions have been studied as a function of oxide concentration, pH, and temperature These authors have shown that an increase in temperature and/or voltage decreases the particle mobility and hence zeta potential The viscosity and conductivity of the various colloidal suspensions increase with an increase of pH and concentration of the suspension Using suitable conditions coherent, well adhering and uniform plated films were obtained with suspension containing Fe_2O_3 , NiO, Cr_2O_3 , and TiO_2

According to these authors oxide powders are not dispersed into their individual particles in a suspension. The size of the aggregate is dependent on the concentration of the suspension, the dispersion liquid, dispersing agent, and pH. The aqueous medium used by Caley and Flengas contained poly acrylic acid as the dispersant and triethylamine as the neutralizing base.

Kucharski⁽¹²⁾ has reported successful electrophoretic deposition of thick WO_3 and Cr_2O_3 coatings from an aqueous suspension containing 22 gms of oxide per 100 cm³ of water. Reportedly, the thick coatings adhere to steel substrate even at high temperatures. Kucharski has been able to carburize the oxide coatings at an elevated temperature, using CO-CO₂ mixture to produce hard and wear resistant surfaces.

Theoretical Background -

When a small particle is suspended in water it normally acquires a charge and would migrate towards one electrode or the other under the influence of an electrical field. Although the phenomenon was observed in 1808 by Reuss and explained qualitatively by Quincke in 1861, it remained for Von Helmholtz⁽¹³⁾ in 1879 to formulate a quantitative theory of electrophoresis. He employed the concept of an electrical double layer at the interface between the solid and liquid phases. A unified theory, which takes into consideration the thermal energy of ions, was proposed simultaneously by Gouy⁽¹³⁾ and Chapman⁽¹³⁾. It is known as Gouy-Chapman theory or 'Diffuse layer theory' of the electrical double layer. Further modifications to theory have been given by Stern⁽¹³⁾.

The electrical double layer consists of a rigid solution layer held adjacent to the solid surface by both electrostatic and specific adsorptive forces. The layer in contact with this surface is then surrounded by a diffused layer. When a suspension of such charged particles is placed in an electric field the particles migrate towards the electrodes depending upon their charge. The movement of particles give rise to a plane of shear near the surface of particles. The laws of viscous flow, which

govern the movement of particles are well known, but there exists some uncertainty about the actual value of the viscosity in the electrical double layer. This is because of the high field strength and the short range interactions between the two planes at the phase boundary.

For solid particles suspended in a liquid it is customary to take these effects roughly into account by assuming the existence of a 'slipping plane' parallel to the actual phase boundary, but displaced somewhat to the solution side of the phase boundary⁽¹⁴⁾. The liquid is assumed to be completely immobile between the phase boundary and the slipping plane and is like the bulk liquid outside the slipping plane. In accordance with this view electrokinetic phenomena would be determined by the outer part of the electrical double layer and more particularly by the potential at the slipping plane, called the electrokinetic potential or zeta potential. The expression for the velocity of particle V , in an electrical field E is

$$V = \frac{A \epsilon z E}{\eta}$$

ϵ and η are the bulk values of the dielectric constant and viscosity respectively. z is the zeta potential.

A is a constant, the value of which is given by Helmholtz as $\frac{1}{4\pi}$ and Smoluchowsky, $\frac{1}{6\pi}$ ⁽²⁾

It is not possible to calculate the rate of deposition of particles at an electrode from above equation or other fundamental properties of the particular system. Some investigators⁽²⁾ have formulated equations co-relating the deposition rate with the current density, concentration, potential gradient, and particle mobility. For example, Hamaker⁽¹⁵⁾ suggested that the amount of material deposited is proportional to the time, the concentration, the surface area, and the electric field

$$\text{The yield, } Y = G, C \iint \frac{dv}{dn} ds dt$$

where C = concentration, G , a constant, which will depend on the chemical composition of the suspension but not on the physical conditions of the experiments. $\frac{dv}{dn}$ is the electric field perpendicular to the surface S

James et al suggested⁽²⁾ that not all suspensions yield an electrophoretic deposit. Very stable, non settling suspensions do not yield a deposition. Generally suspensions of marginal stability are the most suitable for deposition.

Hamaker and Verwey⁽¹⁶⁾ in their study of deposition from suspensions in organic media have found a general parallelism between electrodeposition and the formation of deposit by gravity. This suggests that the deposition at the electrodes is mainly a mechanical

problem, the electric nature of the phenomenon being of secondary importance, the role of the electric field is only to provide a force which moves the particles towards and presses them together on the electrode

CHAPTER III
EXPERIMENTAL APPARATUS AND PROCEDURE

Electrophoretic cell -

The electrode arrangement in the electrophoretic cell is shown in Fig 1 (a,b) The cell consists of a centrally placed copper anode 1.5" x 0.5" and two copper cathodes (2" x 2") There is provision for raising or lowering the electrodes and for changing the spacing The cathodes are fixed to a perspex cover sheet by screws The central anode is held by a clip and, therefore easily replaceable The particular size of the electrodes were arbitrarily chosen after some preliminary measurements The cathodes on either side of the anode are made bigger to ensure uniform deposit on anode, to which the suspended particles are drawn during electrophoresis The electrode arrangement rests in a glass beaker of capacity 500 ml During actual electrophoresis always 250 ml of water was taken which almost covered the electrodes

The electrodes were connected to a variable D C power supply, a milliammeter, and a stabilizer

Materials

(a) Deionized water (D I Water) was prepared in a Branstead deionized water plant mixed resin demineralizer with colour code-red was used The

conductivity of water varied from 2 to 4 micro-mho

(b) Titanium Dioxide

Titanium dioxide was supplied by B & B company Bombay, red brand of two types

Sample A - Particle size ranged from 4 to
(S 1) 7 microns

Sample B - Particle size ranged from 10 to
(S-2) 14 microns after grinding

(c) Acrysol and triethylamine -

In some of the experiments, Acrysol, A-5, Kohn & Haas Philadelphia, PA- 19105 and triethylamine, manufactured by S M chemicals, Baroda were used

Auxiliary equipments -

(a) Rectifier Model GFA, 220 volts, 0-125 V D C 10 Amps, manufactured, Chicago, U S A

(b) Microscope - B and L U S A DM- Series, Magnification- 40 X objective, and 10 X filler micrometer eyepiece

(c) Conductivity meter - Type 303, Sr No -011, Direct reading conductivity meter, Manufactured by systronics, Ahmedabad

(d) pH meter - Model, L1-10, manufactured by ELICO, Hyderabad

(e) Stabiliser - Model GSS 505, Servo Voltage stabiliser, manufactured by Gargya Research instruments, New Delhi

(f) Processor Type No VPB-PI, Serial No - 1007/75,
 Ultrasonic processor, manufactured by vibronics pvt
 limited, Bombay

Experimental procedure

A large numbers of copper strips, properly numbered were made for deposition experiments. These were mechanically polished, degreased and washed using a solution of 10% CeCl_4 , acetone and finally with distilled water. Dust free strips were kept in the desiccator. For any given experiment one of these strips was fixed to the anode clip and the entire electrode system was thoroughly cleaned using dilute acids, distilled water and the D I water. The beaker was cleaned by soap solution, distilled water and then D I water. 250 c c of a suspension with a predetermined concentration was poured into the beaker. The electrode system was inserted in the suspension after addition of predetermined amount of acrysol A-5 and triethylamine. In some experiments the suspension was stirred using a processor or a hand stirrer. During the experiments it was gently stirred.

The deposits were obtained for predetermined conditions. After deposition the anode was removed from the clip and suspended in air in a specially designed rack for drying. After overnight drying this specimen

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was weighed. For the weight gain value and the area of the deposit one could obtain the weight of deposited per unit area.

It was noted that the thickness of the deposit was slightly greater at the lower regions of anode as shown in Fig (7a). This may be attributed to continued settling of the suspension, which leads to higher concentration values at lower depths. The average thickness of the deposit was obtained by microscopic examination.

Knowing the weight and area of deposit, the total thickness of the anode after deposition and the thickness of the copper strip, one could determine the density of the deposit.

In some cases deposits were photographed.

CHAPTER IV

RESULTS AND DISCUSSIONSPreliminary Measurements

Since electrophoresis is extremely sensitive to the electrolytic medium, some preliminary experiments were carried out to examine the nature of the deionized water and oxide suspension.

Using the electrode arrangement discussed in chapter 3, current vs potential graphs were obtained for D I water. Fig 2 shows that the conductivity generally increases with time. Large conductivity of electrolyte is undesirable for electrophoretic deposition due to larger IR losses and gas evolution at electrodes. The gradual increase in conductivity of water with increased time of exposure is possibly due to dissolution of CO_2 from air to form CO_3^{2-} and HCO_3^- ions in solution. This is substantiated by the observation that the conductivity values are restored to original values when an inert gas like N_2 is bubbled through the solution. It has been observed that while it is difficult to get electrophoretic deposits from suspensions in 'degenerated' (due to long exposure to atmosphere) water, good deposits can be obtained again by bubbling N_2 . Fig 3 shows that the current increases with increase in the amount of TiO_2 .

Charged TiO_2 particles contribute to the overall conductivity of the suspension

The effect of the solids content of the suspension, and potential on the current is shown in Figure 4. The current increases both with increase in solids content and voltage.

Effect of Deposition Time on Current -

Figure 5, shows that the current gradually decreases with time. As the thickness of the deposit increases, it will offer greater resistance to current flow. The current is reduced to half of its initial value in about 30 minutes. The conduction after long periods is possibly through the electrical double layer present around each particle. Low density of the deposits obtained in many cases supports the hypothesis that a layer of water is present around the particles when they are electrophoretically deposited.

Kinetics of Deposition -

Fig 6 shows some data on kinetics of deposition. Fresh suspension was used for each experiment. The thickness of the deposits and the amount deposited per unit area increases continuously with time. The density of the deposit however is rather low (0.5 to 1). It should be noted that the density of TiO_2 is 3.8. The

density values were measured after drying overnight the specimens at room temperature. It appears that the initial deposits contained a large amount of water. Electrochemical deposits containing as much as 90% water have been observed. (5)

Effects of Titanium Dioxide --

Figure 8, shows the effect of the amount of TiO_2 on the thickness, yield and density of the deposit. Both the thickness and amount deposited per unit area increase almost linearly with time, the deposition rate can be enhanced by increasing the amount of TiO_2 . The density of the deposit, however, is maximum at 10 gms/250 cm^3 of water.

Photograph 7 (a) shows the deposits immediately after their removal from the cell. The amount of TiO_2 varies from 5 gm to 30 gm /250 cm^3 H_2O for sample numbers 1 to 5 (details are given in the figure captions).

Photograph 7 (b), shows the same deposits after drying overnight. Cracks appeared in deposits 3, 4, and 5 after drying. By visual examination deposit number 2 was found to be coherent and uniform.

Effect of potential on quality of the Deposit -

Figure 9, shows effects of variation of voltage on the nature of deposits for a given concentration of suspension. It is found that increase in the voltage increases both the thickness and the amount of deposit per unit area. The experimental values were obtained on two different days. The discontinuity in data may be ascribed to the slight difference in the conductivity of the D I water.

Similar experiments were repeated using voltage variation over a range of 0 -150 V, and different amount of TiO_2 . Three sets of results are shown in figures 10, 11, and 12.

Figure 10 shows that the thickness and yield of the deposit increase upto 40 V and then levels off. The increase in the amount TiO_2 to 10 g or more/ 250 cm³ H₂O improves the thickness and yield of the deposit as shown in figs. A value of 10 g/cm³ was the largest density obtained under these conditions. In all the cases it is found that below approximately 40 V, the properties are poor and it is also seen that deposits had poor adherence due to an insufficient potential gradient for proper electrosmosis. It was noted that in

Figures 10 c, 11 c, and 12 c density reached the value maximum around 40 V and then almost levelled off

From these figures it is to be noted that at larger TiO_2 concentrations significantly large yields were obtained. The density at 40 V in Fig 11 c is larger than that in Fig 10 c. The deposit was ~~coherent~~ and smooth. When the TiO_2 content was increased to 20 gms, Fig 12 c no significant increase in density was observed. Therefore, 10 gms of TiO_2 and 40 V was taken as the optimum condition for deposition.

Effect of Sodium Pyrophosphate -

Preliminary measurements showed that coarser particles tend to sink and, therefore are not available for deposition. Constant stirring would prevent settling out it is not desirable, however, since it is likely to interfere with the deposition process.

An attempt was made to stabilize the suspension with the addition of a small quantity of sodium pyrophosphate, which is known to be surface active reagent.

Sodium pyrophosphate decreased the amount of TiO_2 deposited as shown in fig 13. A little bit pitted and / or even nodular deposits were obtained at lower amount and at higher amount, thin pitted deposition resulted. Most of the places remained undeposited.

Effect of suspension pH -

The results reported so far were suspensions in plain D I water, with pH of about 7. Effect of pH has been investigated with addition of triethylamine or triethanolamine to increase the pH and by addition of phenol or acrysol to decrease it. Inorganic acids and alkalies such as HCl, H_2SO_4 and NaOH etc cannot be used because they make the electrolyte highly conductive and unsuitable for electrodeposition.

Acrysol is a high molecular weight acidic polymer. It is often preferred in electrophoretic work for its role in producing more stable suspension and cohesive coatings⁽⁵⁾. Figure 14, shows the effect of pH variation of the suspension by adding acrysol. pH decreases with addition of acrysol.

Figure 15, shows the variation of thickness, yield and density with the amount of acrysol added. It is to be noted that 1 gm of acrysol, in 250 cm³ of water gives optimum amount for deposition. The deposits obtained by adding acrysol had smooth surface but having bluish in color, due to dissolution of copper ions in the solution and forming metallic complex with acrysol.

Effect of Acrysol and Triethylamine -

It was considered that the beneficial effects of acrysol are not entirely realized because of

the decrease in pI associated with acrysol addition. The solution pH was increased, in steps, by suitable addition of triethylamine and the deposition characteristics are plotted in Fig 16. This figure shows that the electrophoretic deposition process improves as the suspension pH increases from 4 to 7. Further increase in pH is detrimental to the process. This process is best when the pH is about 7, i.e. when the free hydrogen or hydroxyl ion concentration is at a minimum.

Another series of experiments have been conducted with 1 gm of acrysol per 250 cm³ of D I water together with sufficient amount of triethylamine to give the suspension a pH of 7. Some of the results are shown in figure 17, and 18. Figure 17 shows that increasing amount of suspension concentration improves thickness and yield. And density gets a peak value around 10 gms / 250 cm³ water suspension and then levelled. Again for a given suspension concentration viz, 10 gms per 250 cm³ of water, thickness and yield increases with time as shown in Fig 18.

It, therefore, appears that relatively dense and uniform deposits are obtained with a combination of acrysol, triethylamine using an optimum time of 60 seconds and suspension concentration of 10 gms/ 250 cm³ of water.

The maximum density of the deposit
that we could obtain is 2.9 as shown in Table- 1

TABLE -1

| Sl No | Sample | Time (mins) | Suspension Conc gm/250 cm ³ | Voltage (V) | Current (mA) | Conductivity (Mno) | Density g/cm ³ | |
|-------|--------|-------------|--|-------------|--------------|--------------------|---------------------------|-----|
| 1 | A | 6 9 | 2 | 10 | 40 | 25 | 50 | 2 9 |
| 2 | B | 6 9 | 2 | 10 | 40 | 30 | 80 | 2 1 |
| 3 | B | 7 0 | 2 | 10 | 40 | 40 | 88 | 2 7 |

Basic media - Triethylamine

Acidic media - Acrysol (A-5)

CHAPTER-- V
CONCLUSIONS

The following are the conclusions on the basis of investigations reported in this thesis

(i) It is possible to deposit fine particles of TiO_2 (4 to 12μ) on a copper substrate from an aqueous suspension provided deionized water is used. The water medium has a tendency to absorb atmospheric CO_2 which increases the conductivity and renders the medium unsuitable for electrophoretic deposition. This CO_2 can, however, be removed and conductivity restored to initial values by flushing the suspension with an inert gas such as N_2

(ii) The current through the aqueous suspension increases with increase in voltage (at constant solids content). At fixed voltage, it gradually decreases with time because of increased resistance of the deposit layer. The conduction through the deposit layer is apparently due to conduction through the electrical double layer around TiO_2 particles. the

(iii) The thickness and the yield of/deposit (weight/ area) increases with time, when the voltage and suspension concentration are kept constant. Other

factors remaining constant, the thickness and yield also increase with voltage and suspension concentration. The density of the deposit increases initially and then levels off. The density of deposits obtained under ordinary conditions are 0.3 to 1 gm/cm³ compared to the density of pure TiO₂ 3.8. This shows that more than 75% of the deposit is water, which is removed on drying.

(iv) No distinct advantage is gained by adding sodium pyrophosphate which ^{was considered} is believed to be a surface active reagent for TiO₂.

(v) The thickness and the yield of the deposit decrease both at high and low pH values, the optimum condition being achieved between 6.5 to 7.

(vi) Acrysol, which is a polyacrylic acid, decreases the pH of the suspension. If the pH is increased to 7 by addition of a suitable alkali such as triethylamine, coherent and dense deposits are obtained. The improvement in the deposit quality is attributed to the presence of the adsorbed polymer. Approximately 1 gm of A-5 in 250 cm³ of water has been found to be the most suitable.

(vii) Good deposit at room temperature have been obtained under the following conditions -

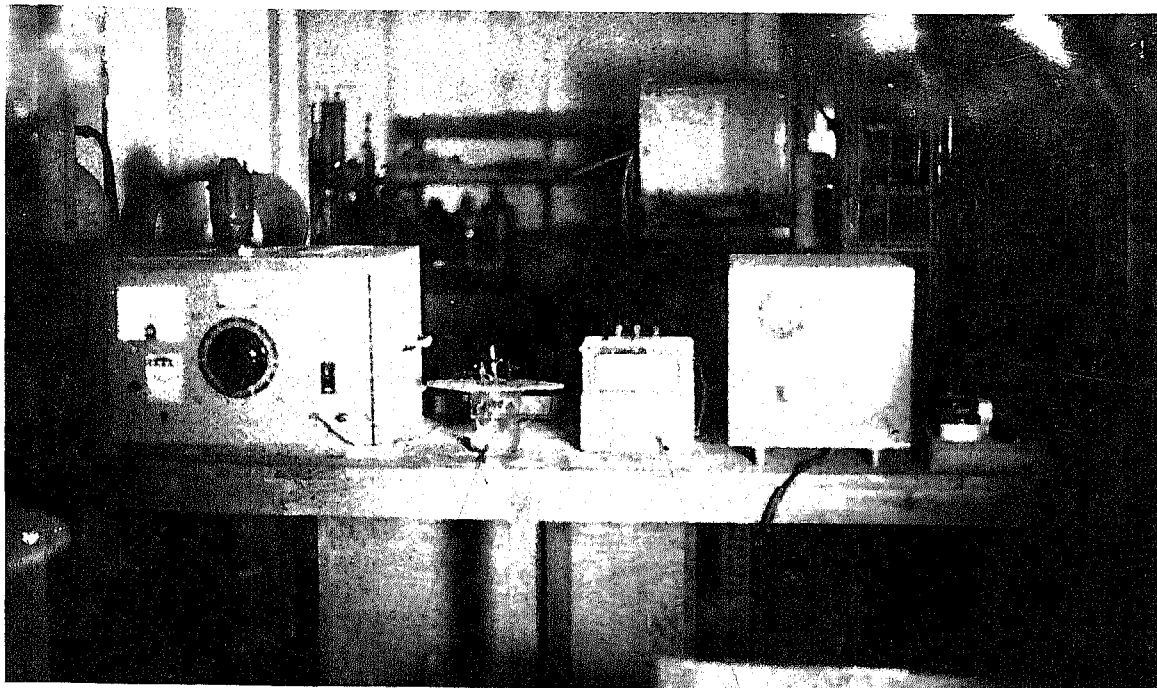
- (a) Amount of TiO_2 - 10 gms in 250 cm^3 of water
- (b) Voltage -40 V
- (c) Time 60 Seconds
- (d) Amount of A- 5--1 gm in 250 cm^3 of water
- (e) pH (adjusted by HFA) - 7

The density of the Deposits obtained under the above conditions is better than 2 The deposits were coherent, smooth, uniform, and showed little tendency to crack after drying

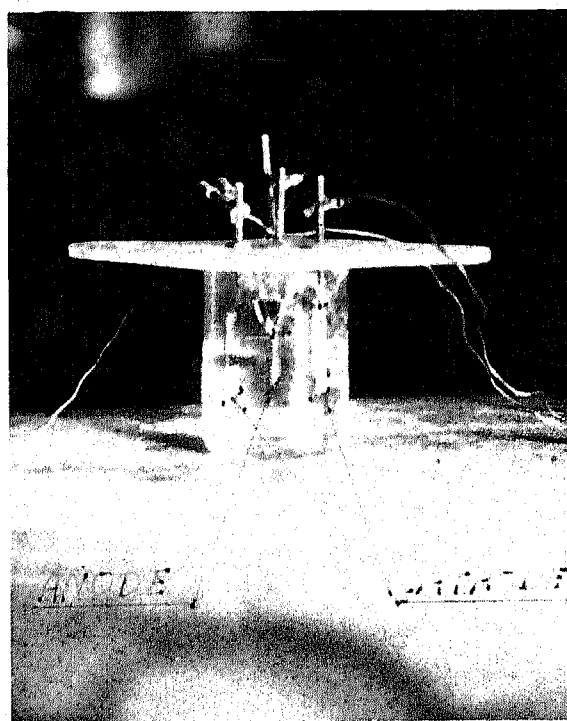
REFERENCE

- 1 Alexander and Johnson, Colloid science, oxford University Press, (1949).
- 2 James J Shyne and Howard G Schneible Electrophoretic Coatings, 34, Modern Electroplating, Ts section
- 3 J H Deboer, H C Homaker, and E J W Verway, Rec Tran Chem 38, 662 (1939)
- 4 Calcy l and Flengas S H Dept of Metallurgy and Materials Science, University of Toronto, Ontario May 1975
- 5 Calcy W F and Flengas S H Electrophoretic properties of the oxides NiO , Fe_2O_3 , Cr_2O_3 , In_2O_3 and TiO_2 in aqueous suspensions May 1975
- 6 ———, U S Patent 2,858,256 (1953)
- 7 J Benjamin and A B Osborn, Trans Faraday Soc 26, 287 (1940)
- 8 S Sencroff and W L Reid, Jr U S Patent 2,843, 541 (1958)
- 9 A C Werner and J J Abbson, ' Preparation of Protective Coatings by Electrophoretic methods' WADC Tech Rept 58- 11 (Feb 1958)
- 10 Guthierrez, C P , Mosley, J R , and Wallace, T C , J Electro Chem soc , Vol 109, No 10, (1962)
- 11 H A Fisch, J Electro Chem Soc , Vol 119, No 1 (Jan 1972)

- 12 A S Kucharski, ' Deposition of Tungsten Carbide surface Coatings' Totorto University
- 13 Antipov, L I, Theoretical Electrochemistry , Mir Publishers, Moscow (1972)
- 14 Electrophoresis- Theory, Methods and applications, Edited by Bier millan, AP INC, New York 1959
- 15 H C Hamaker, Trans Faraday Soc 36, 279 (1940)
- 16 H C Hamaker, and E J W Verway, Trans Faraday Soc 36, 180 1940
- 17 Mercousis, S A , electro deposition of Resin, Depart ment of Chemical Engineering and applied Chemistry, University of Toronto (1969)



1 (a) Experimental Apparatus.



1 (b) Electrophoretic Cell.

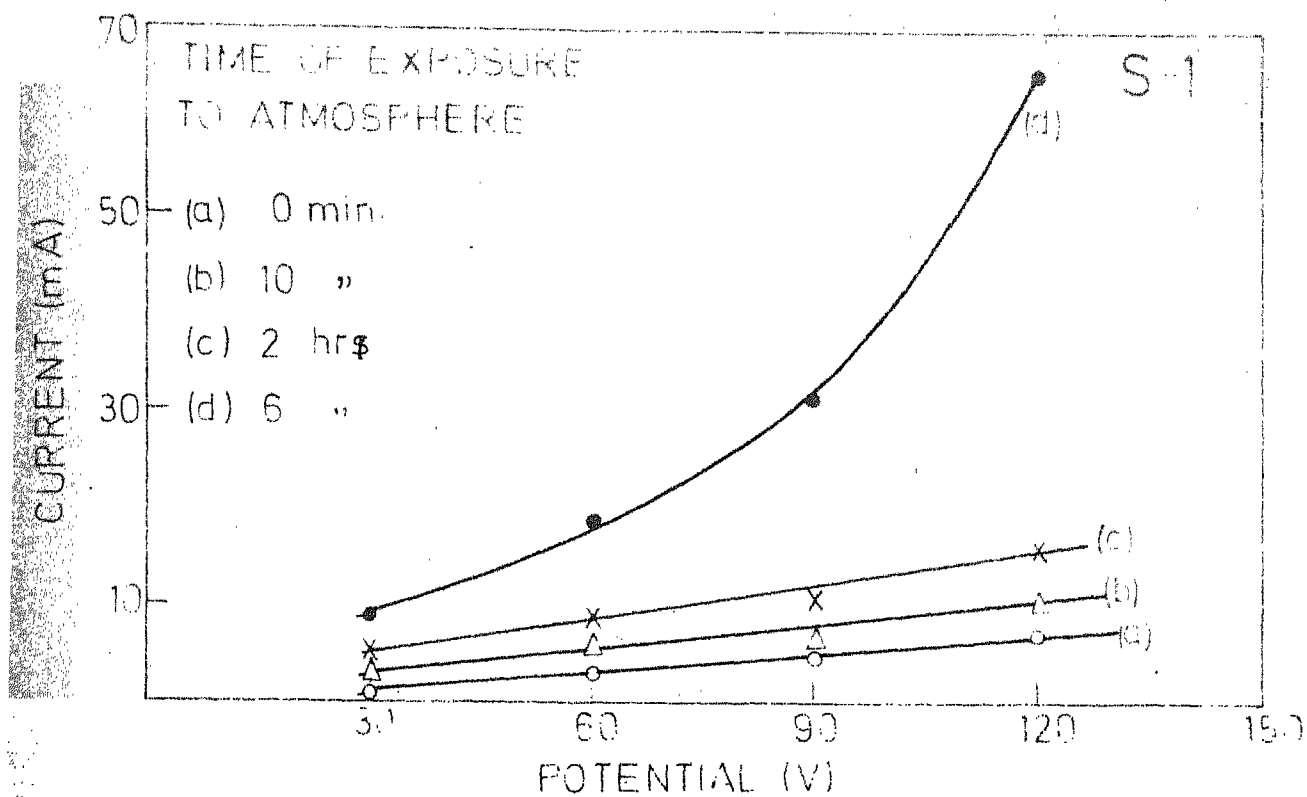


FIG.2 POTENTIAL-CURRENT CURVES FOR DI WATER

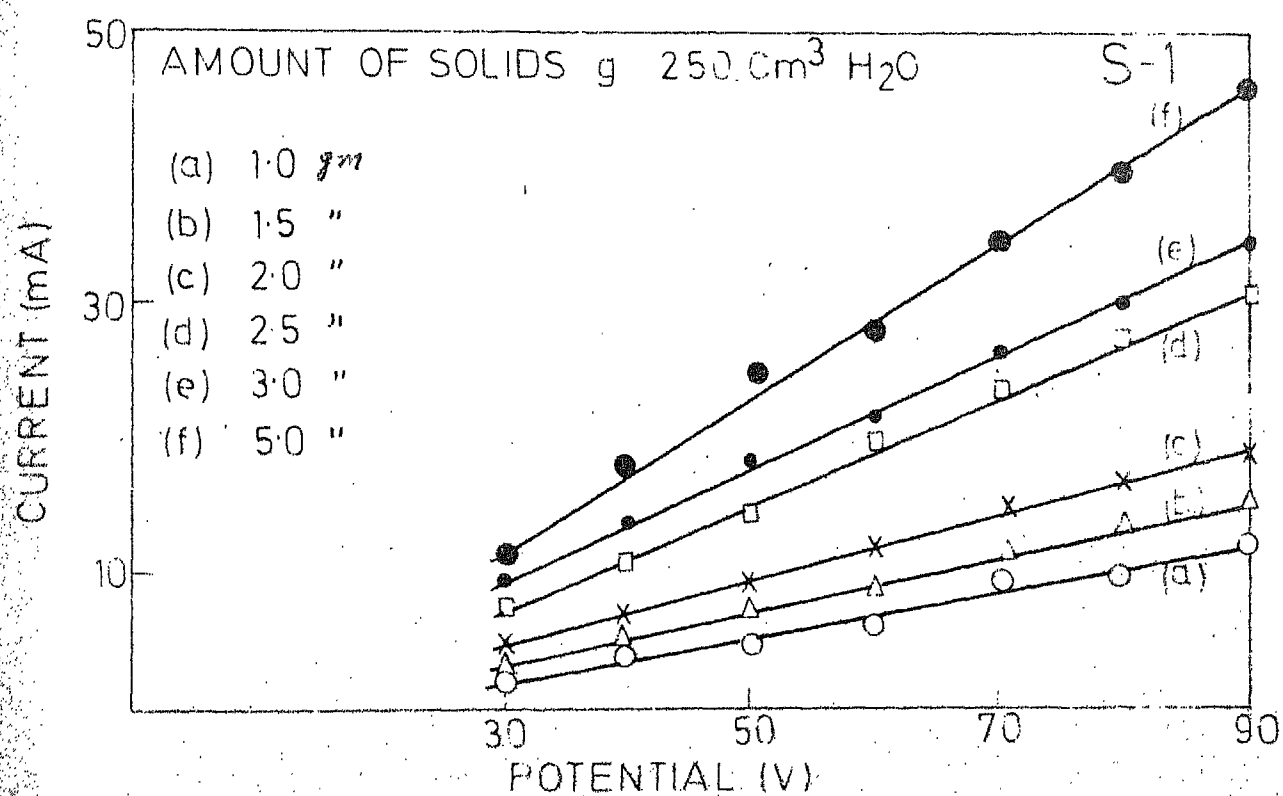


FIG.3 POTENTIAL-CURRENT CURVES FOR TiO₂ SUSPENSION

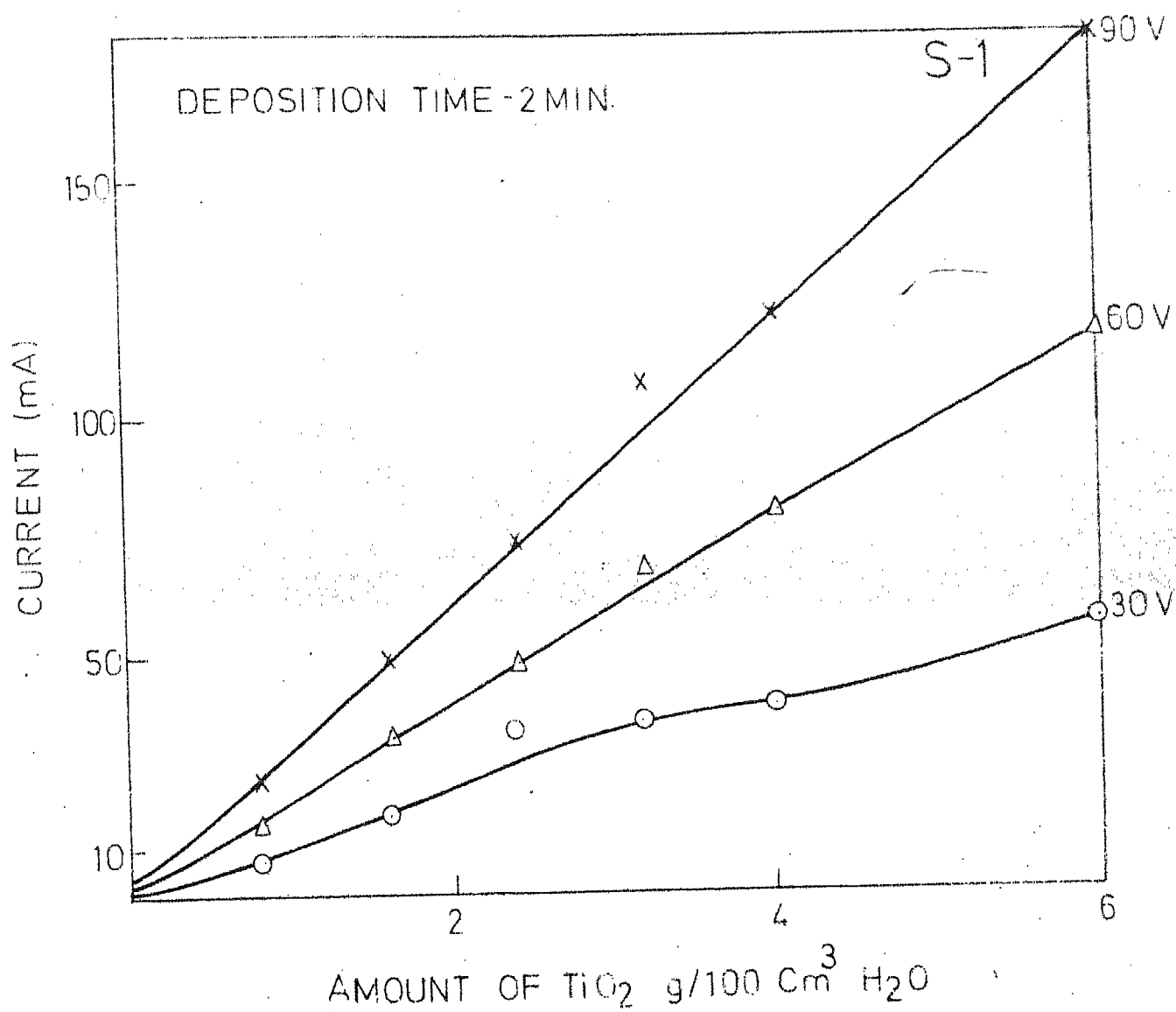


FIG.4 CHANGE OF CURRENT AS A FUNCTION OF AMOUNT OF TiO_2 AT DIFFERENT POTENTIALS

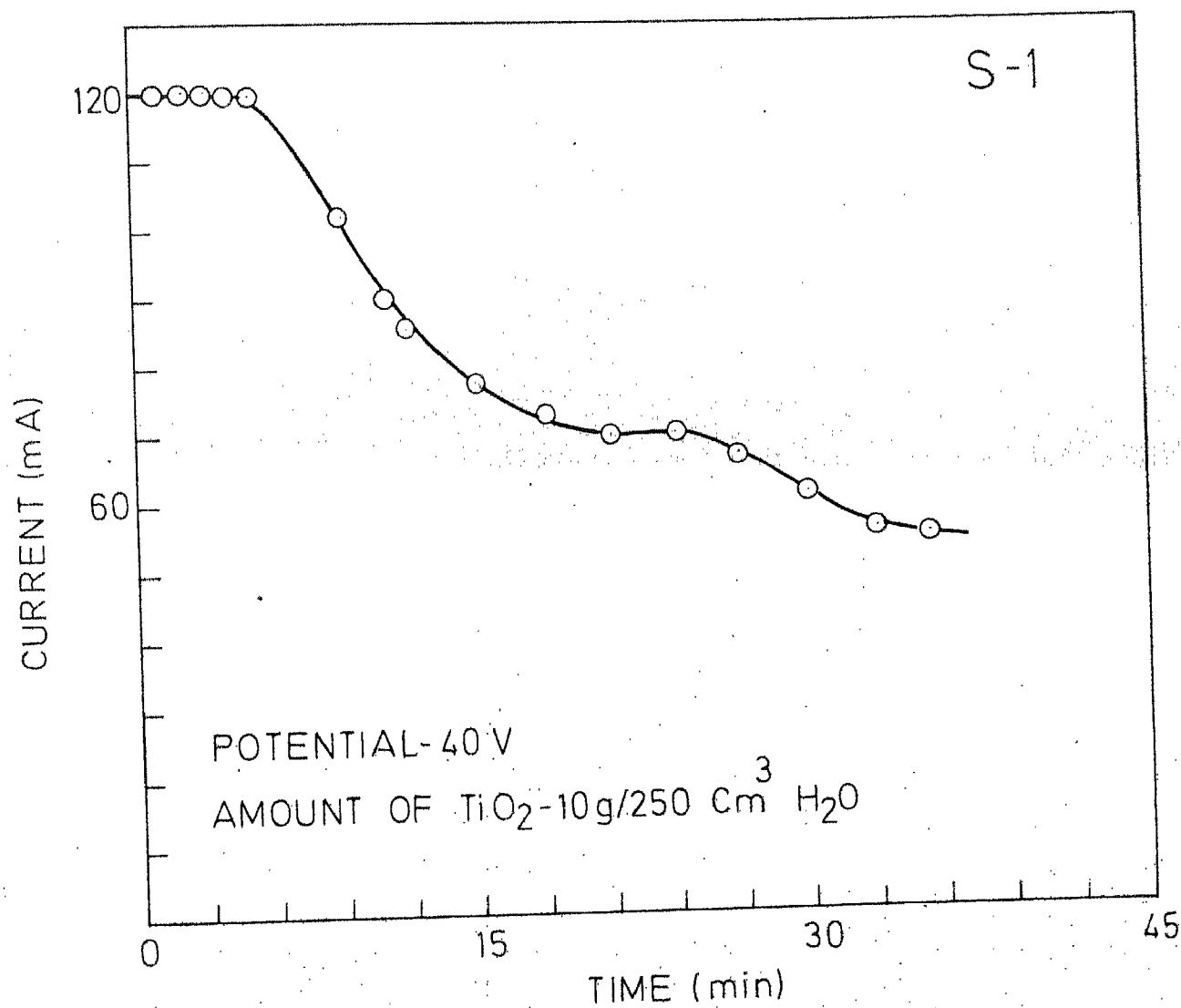


FIG.5 VARIATION IN CURRENT DURING ELECTROPHORETIC DEPOSITION

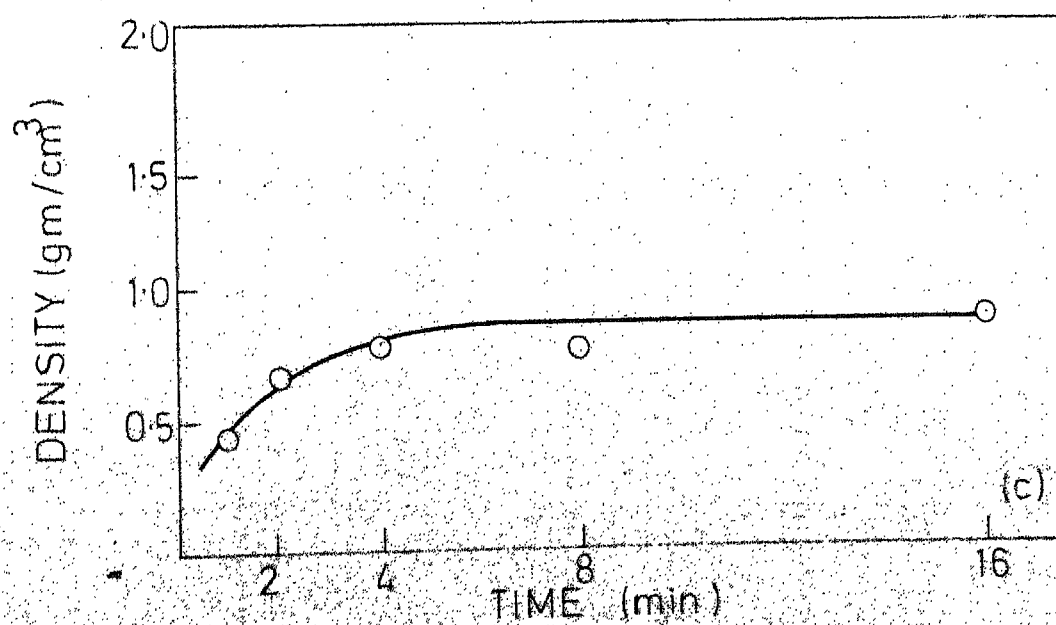
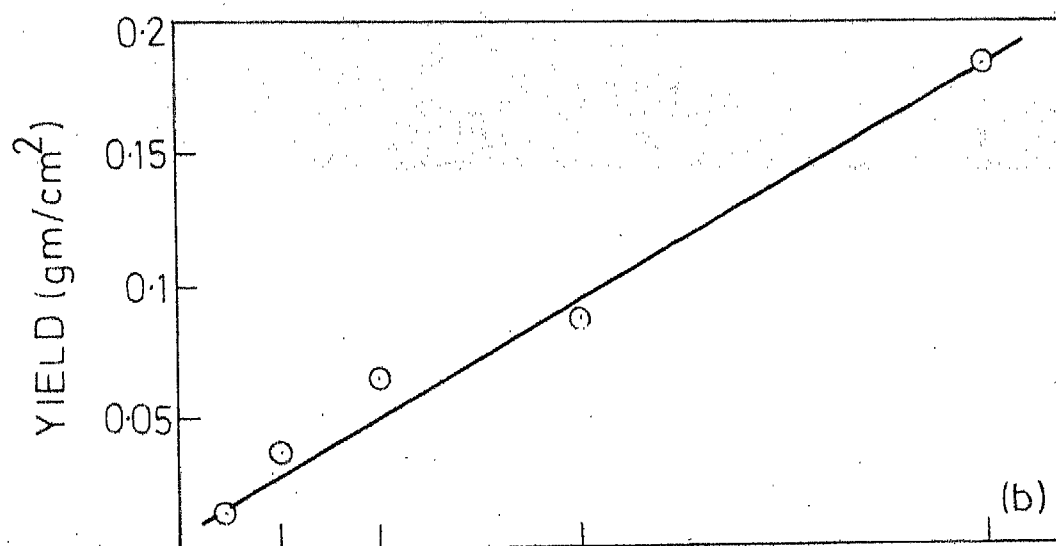
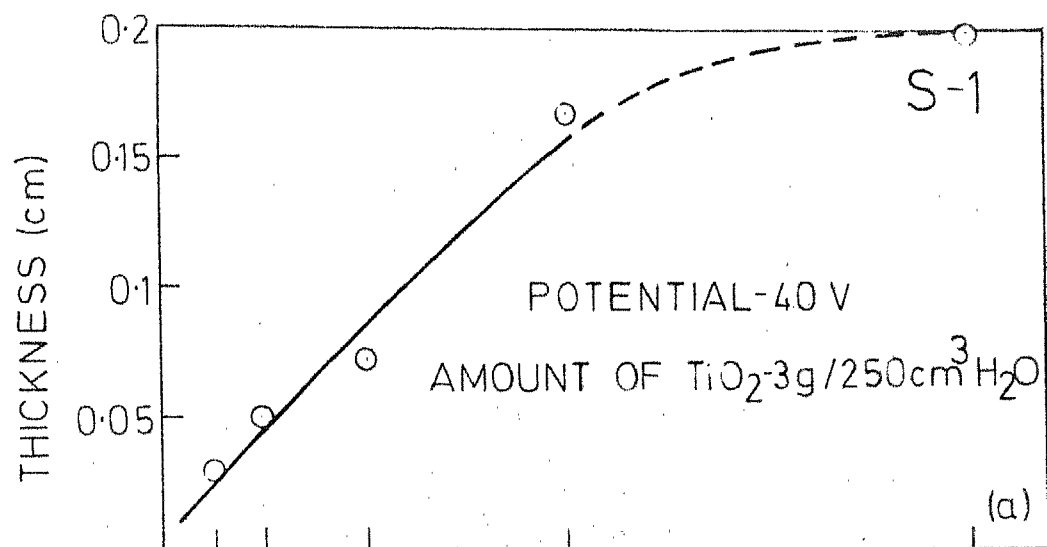
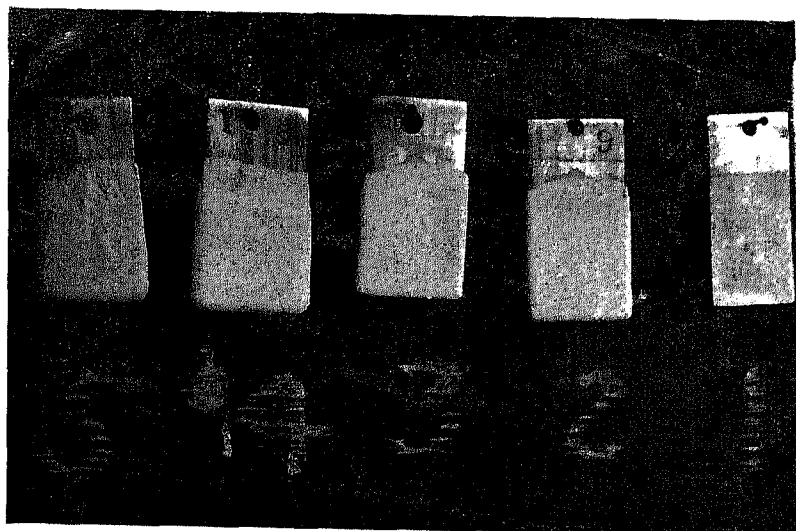
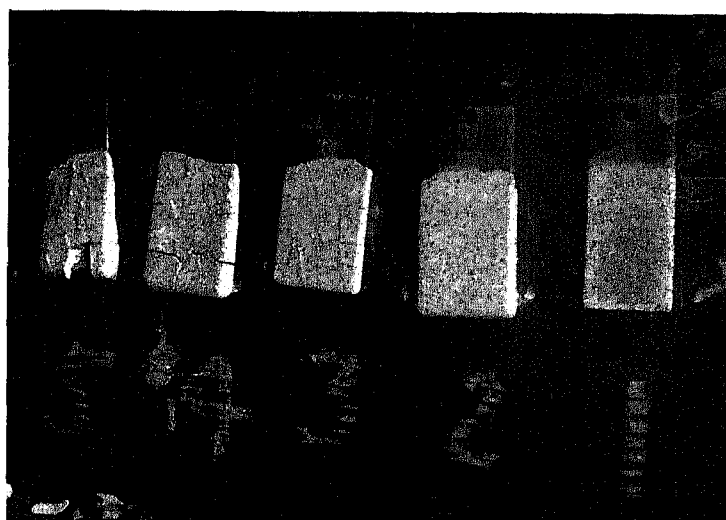


FIG.6 VARIATION OF THICKNESS, YIELD AND DENSITY WITH DEPOSITION TIME



7 (a) Photographs of as deposits



7 (b) Photograph of the deposits after drying.

Nos. 1- 5 gm, 2- 10 gm

3-15 gm, 4- 20 gm, 5- 30 gm/250 cm³ H₂O

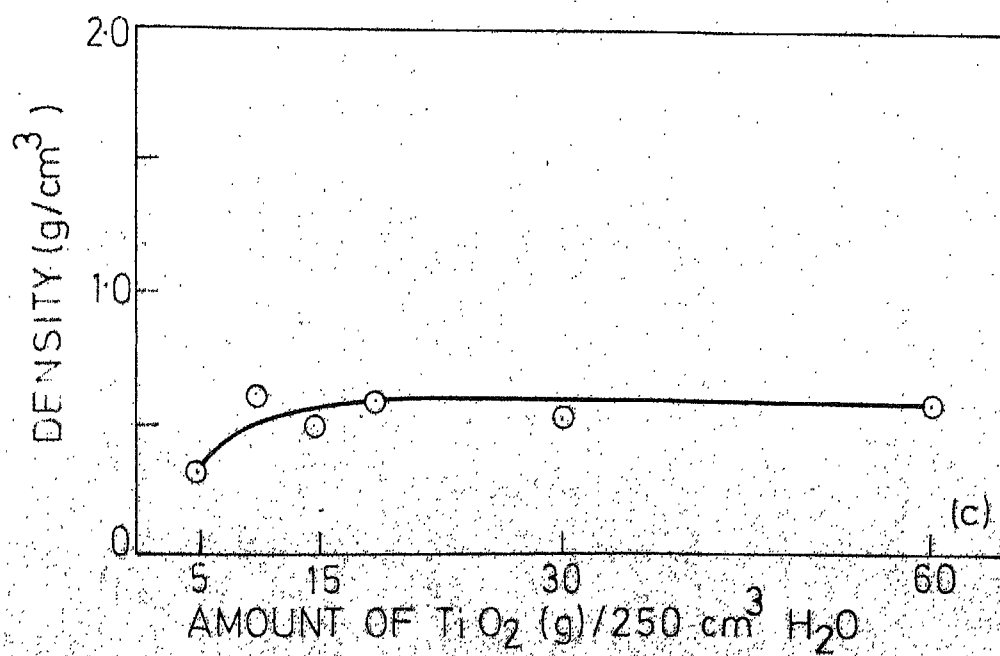
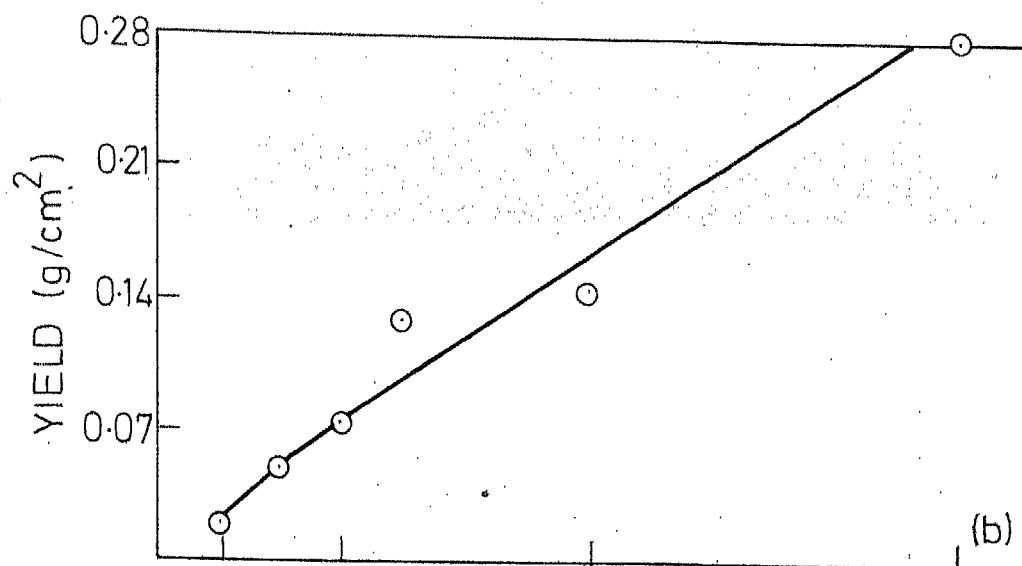
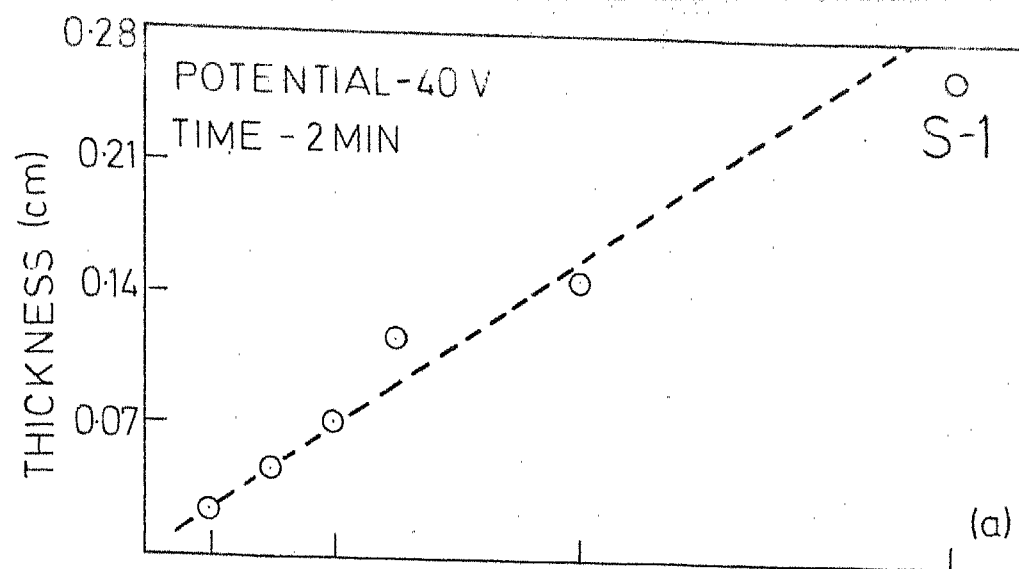


FIG.8 VARIATION OF DENSITY, THICKNESS AND YIELD WITH CONCENTRATION OF THE SUSPENSION

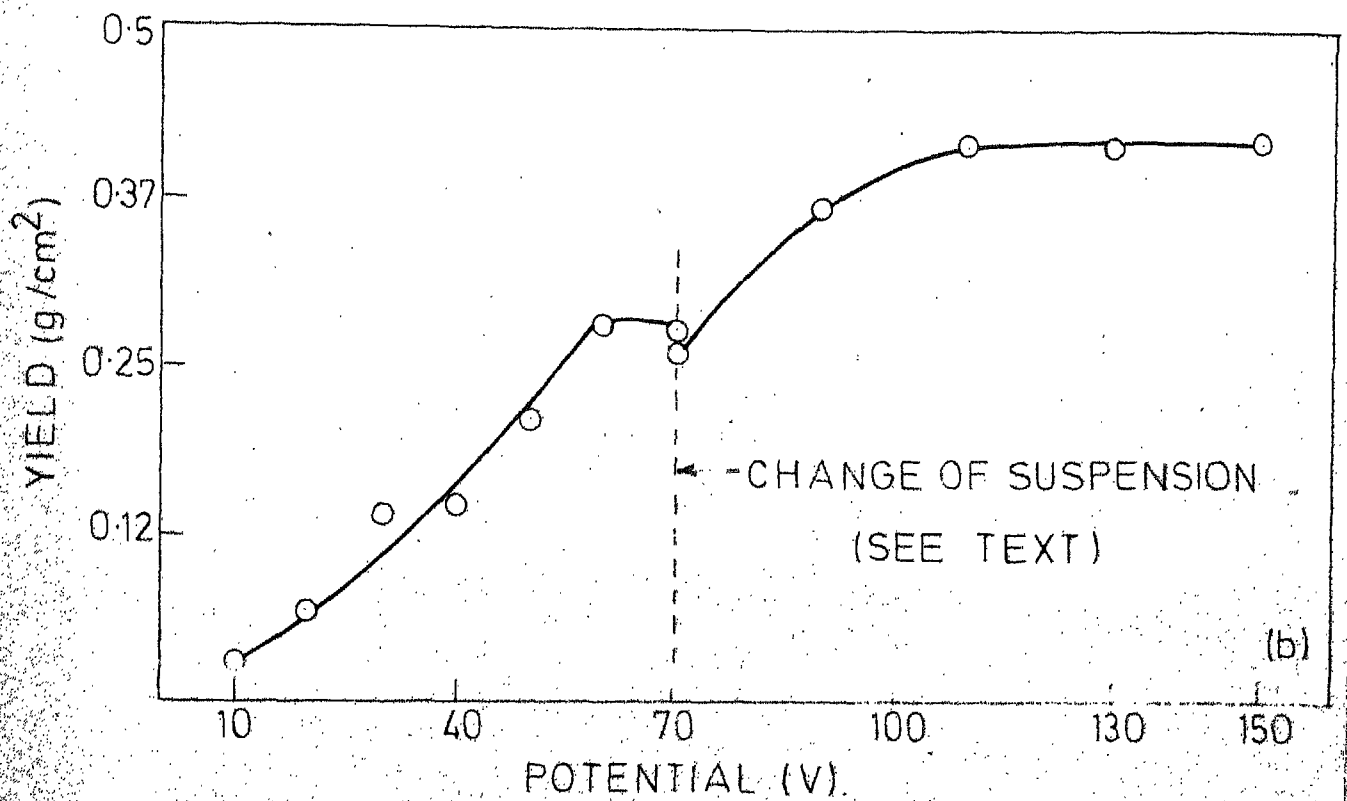
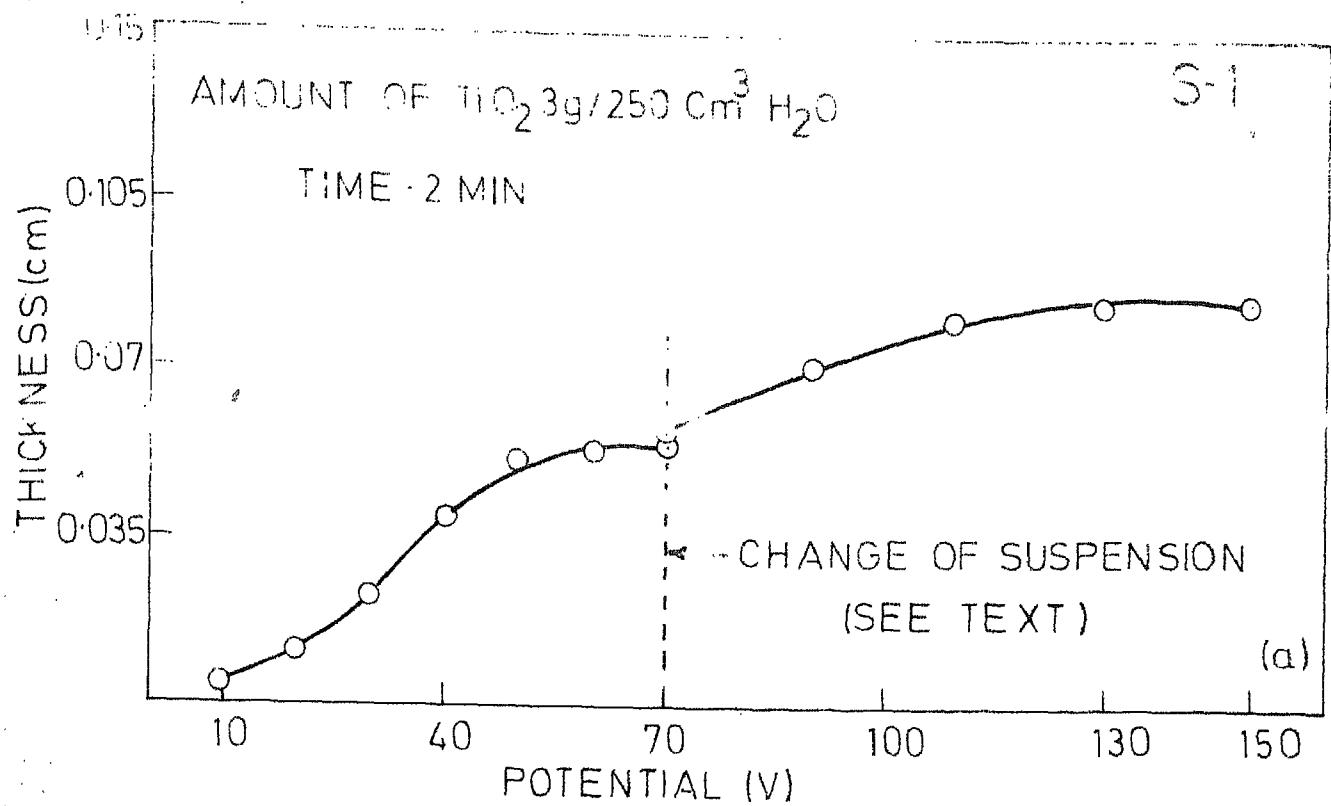


FIG.9 VARIATION OF THICKNESS AND YIELD WITH POTENTIAL

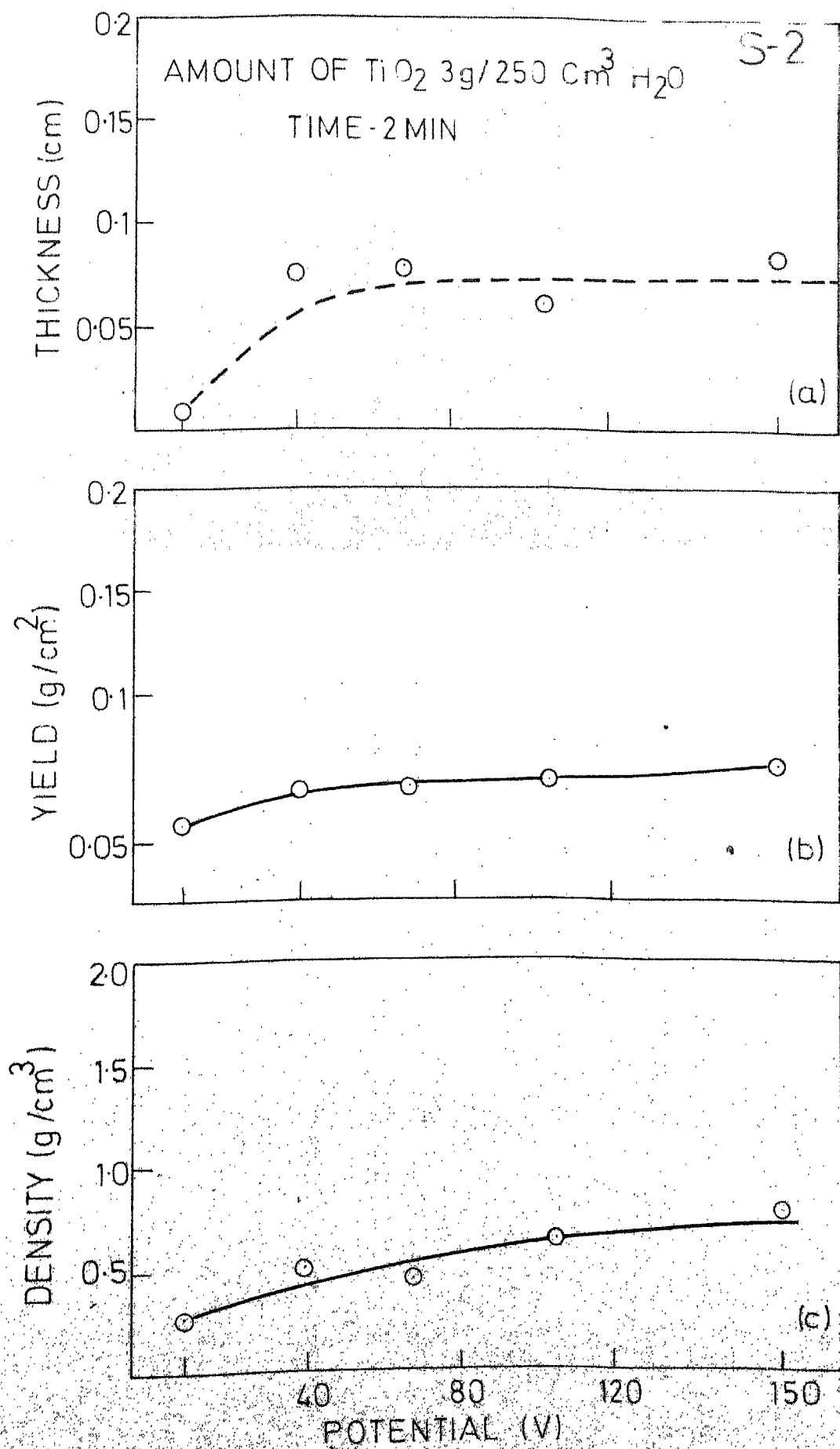


FIG.10 VARIATION OF DENSITY, YIELD AND THICKNESS OF DEPOSITION WITH POTENTIAL

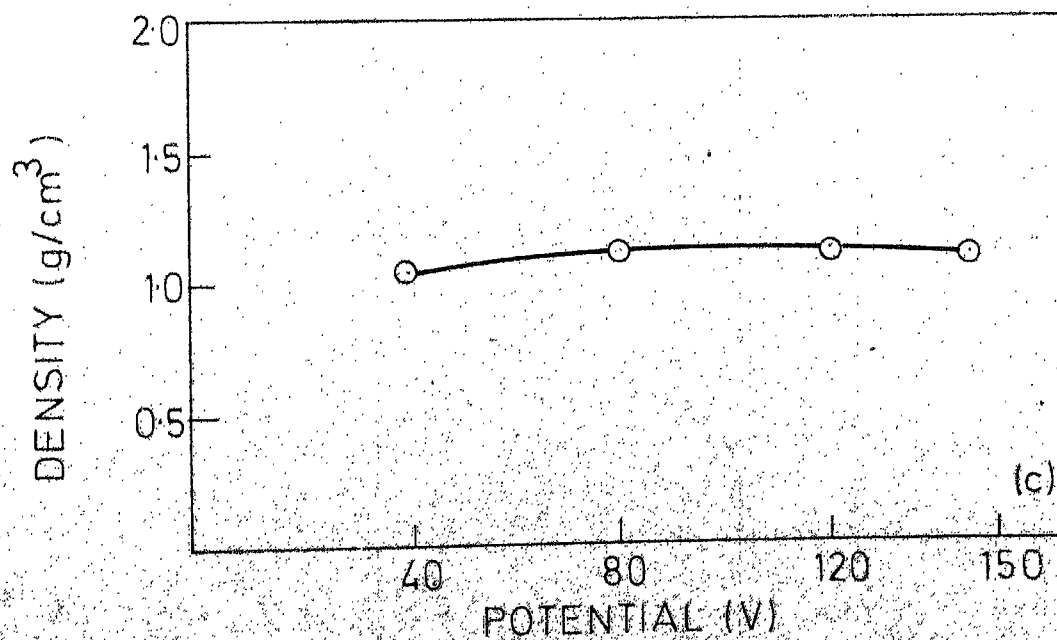
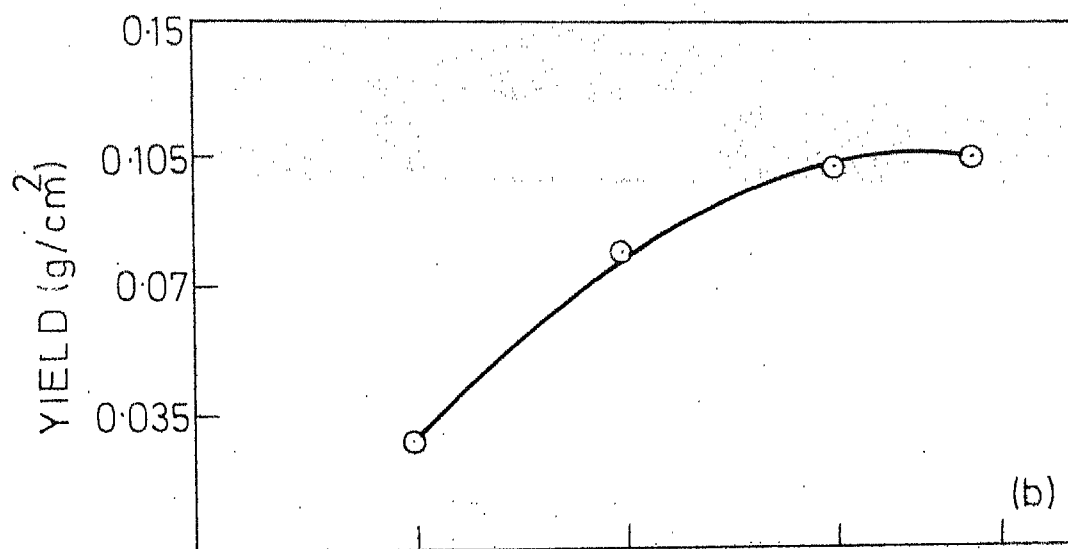
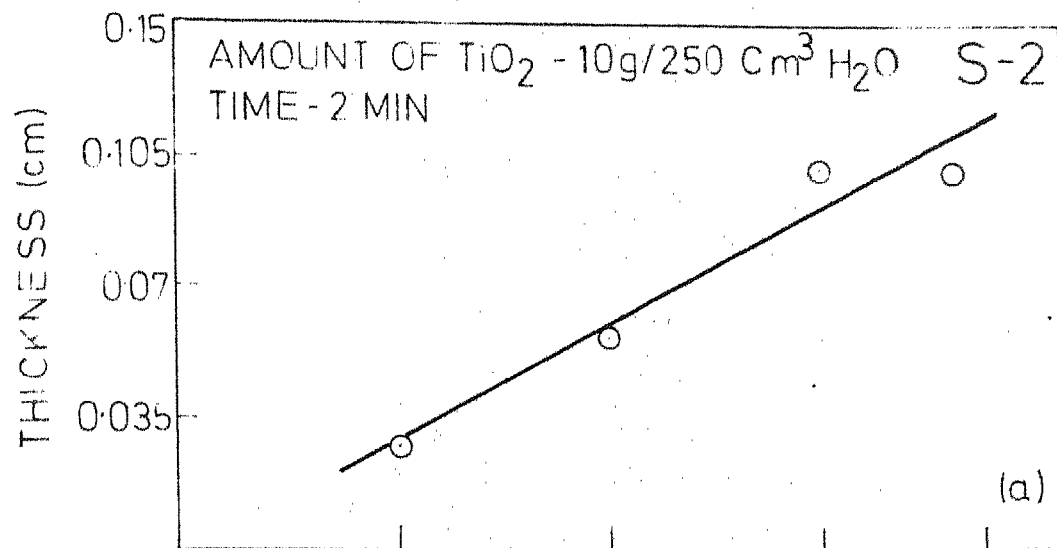


FIG.11 VARIATION OF DENSITY, YIELD AND THICKNESS WITH POTENTIAL

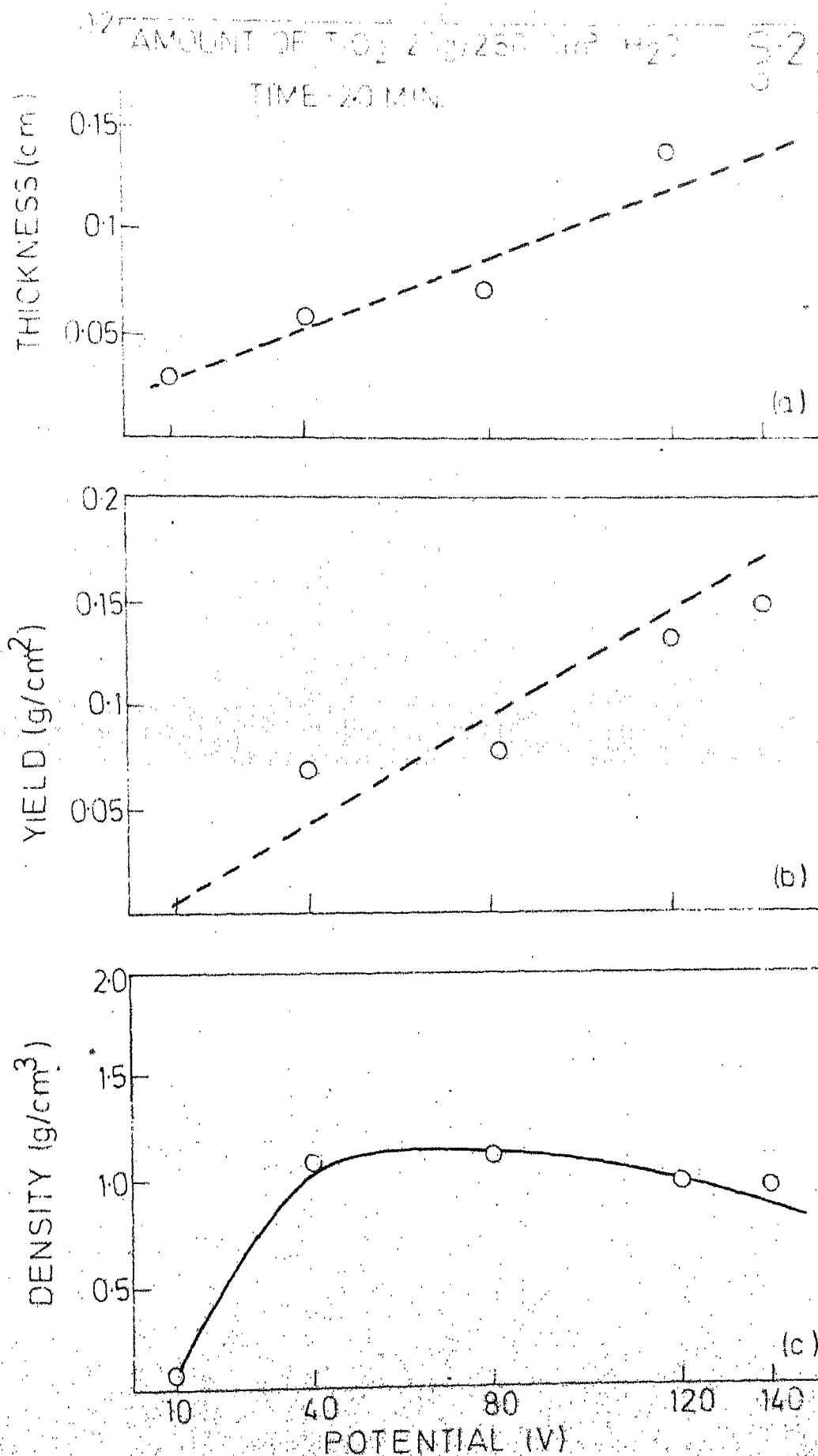


FIG.12 VARIATION OF THICKNESS, YIELD AND DENSITY WITH POTENTIAL

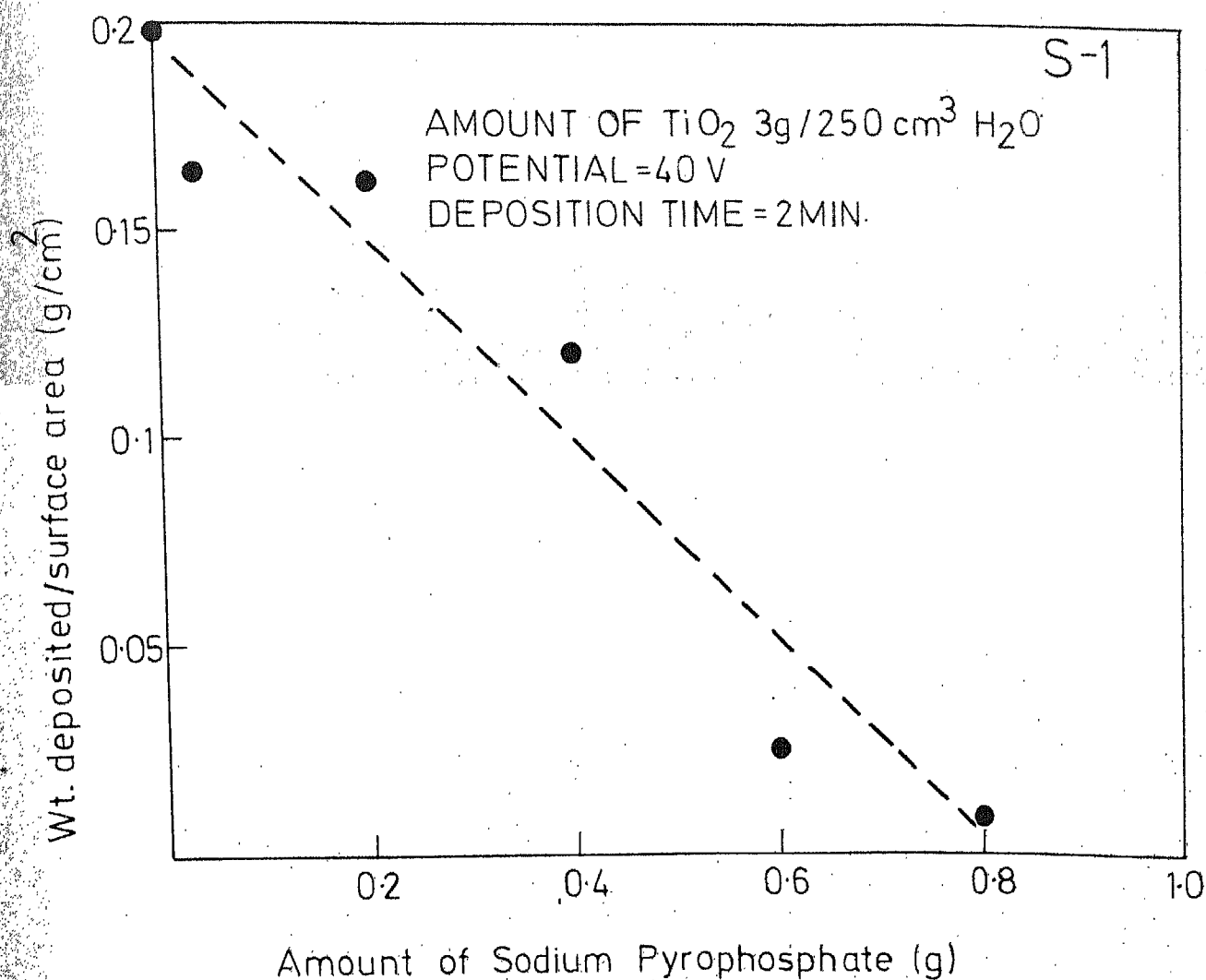


FIG.13 INFLUENCE OF SODIUM PYROPHOSPHATE ADDITION ON ELECTROPHORETIC DEPOSITION

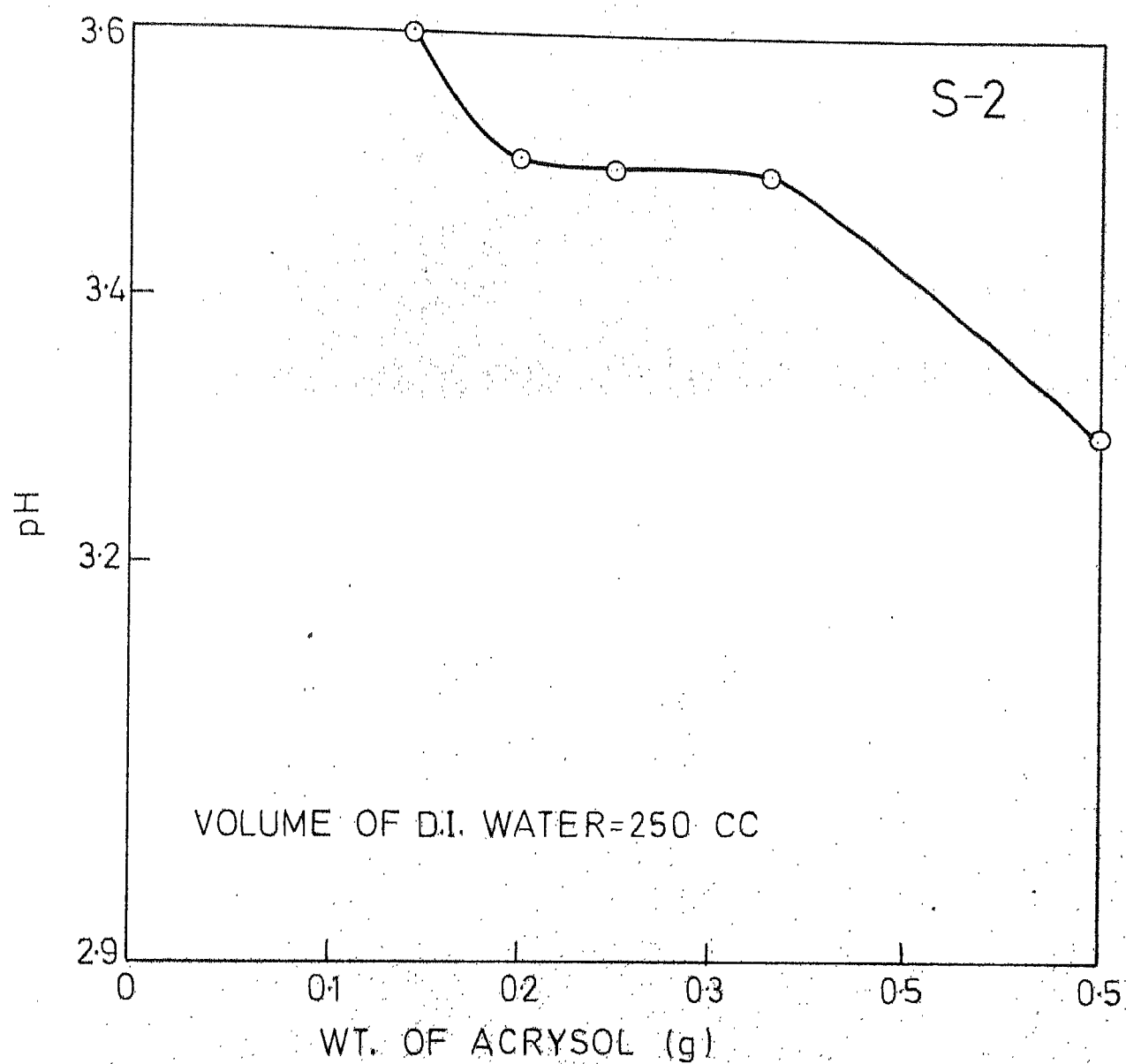


FIG.14 VARIATION OF pH WITH ACRY SOL

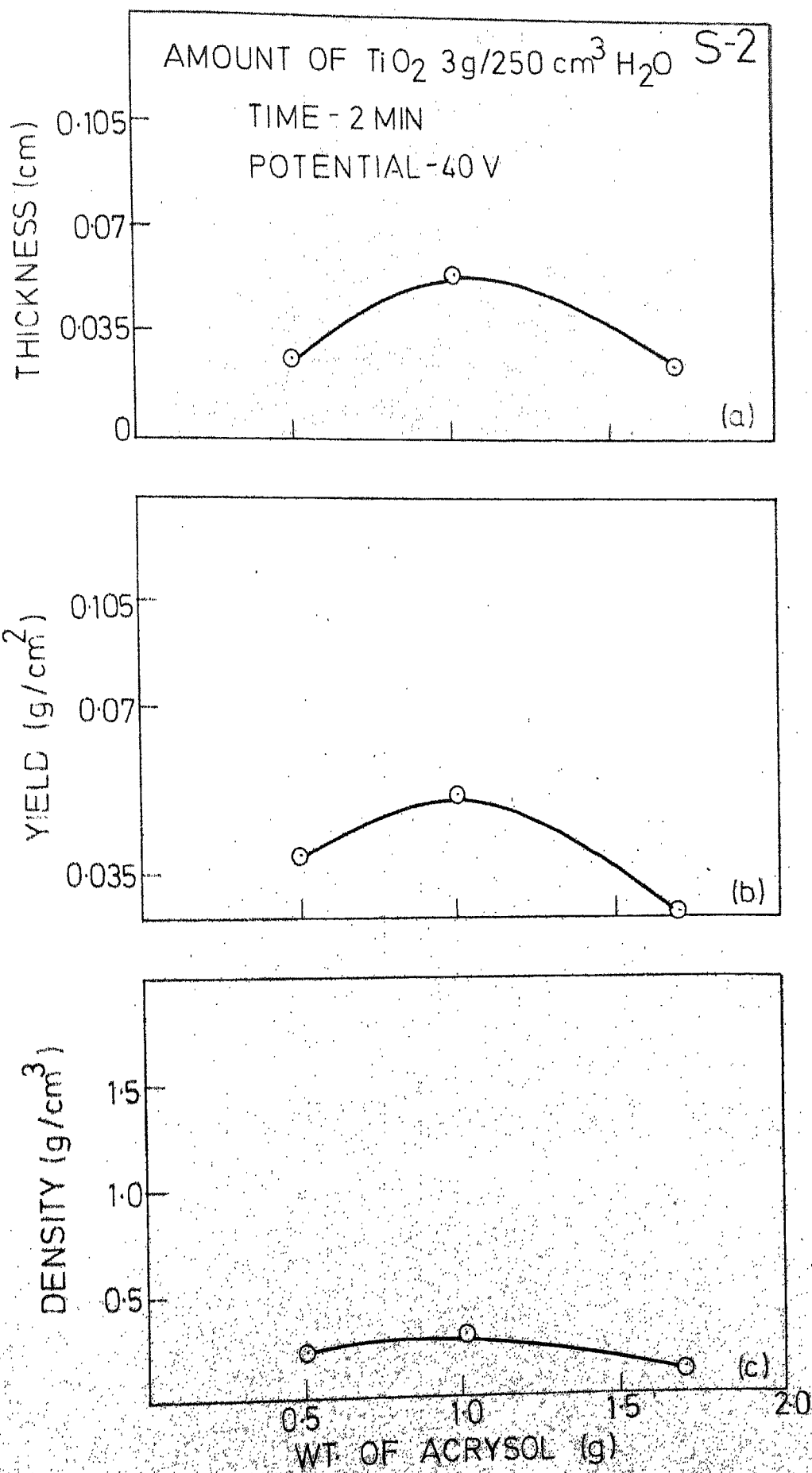


FIG.15 VARIATION OF THICKNESS, YIELD DENSITY WITH ADDITION OF ACRY SOL

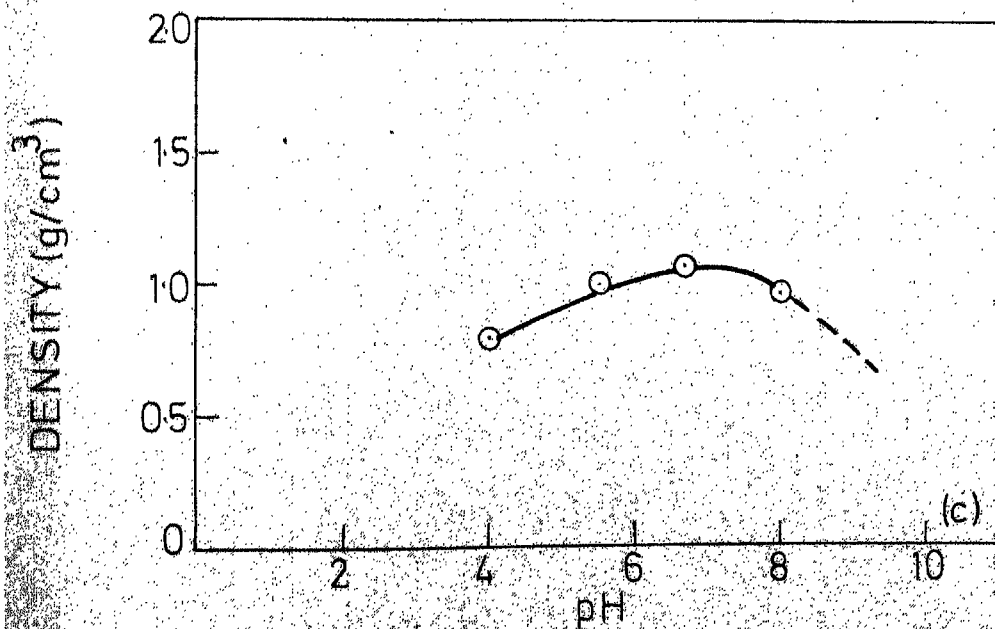
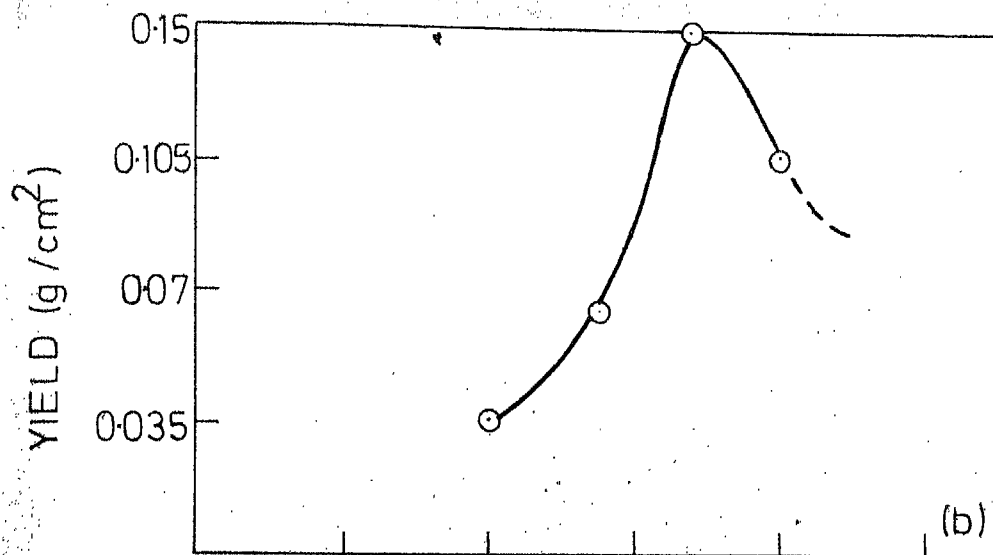
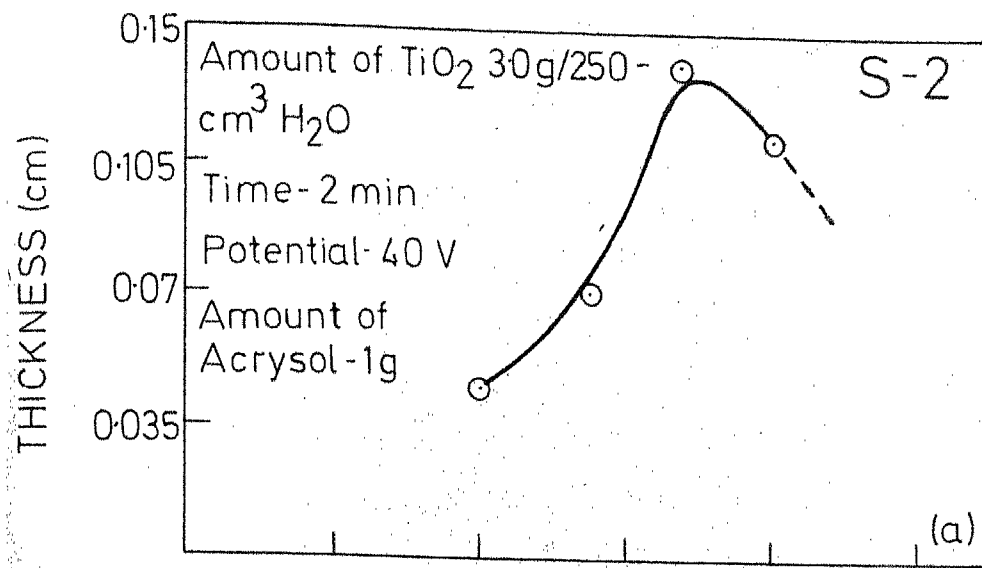


FIG.16 VARIATION OF DENSITY, YIELD AND-
THICKNESS WITH pH OF SUSPENSION

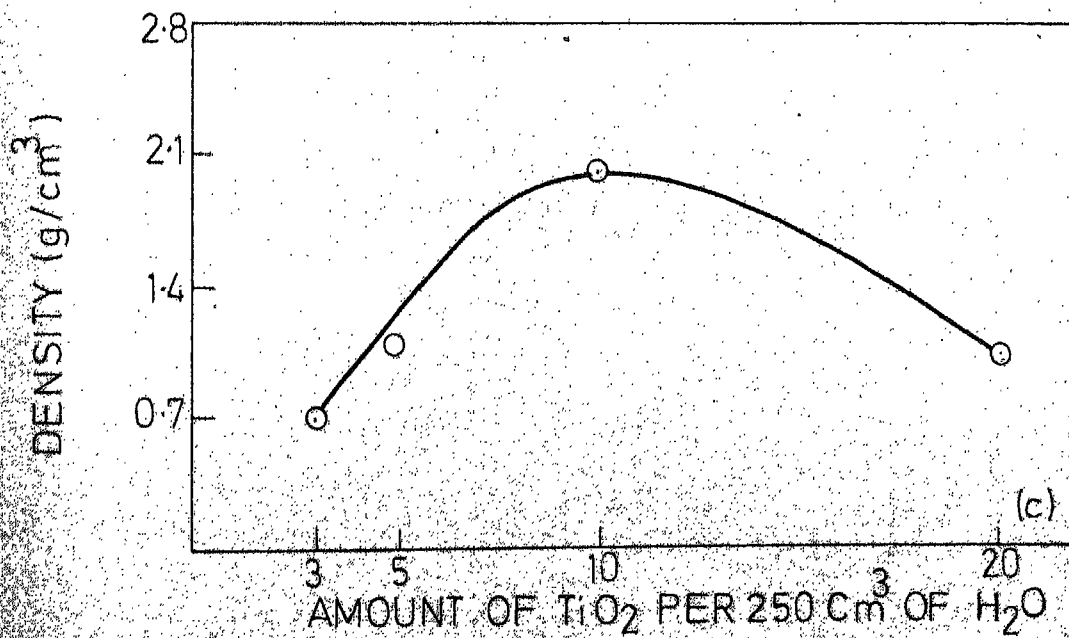
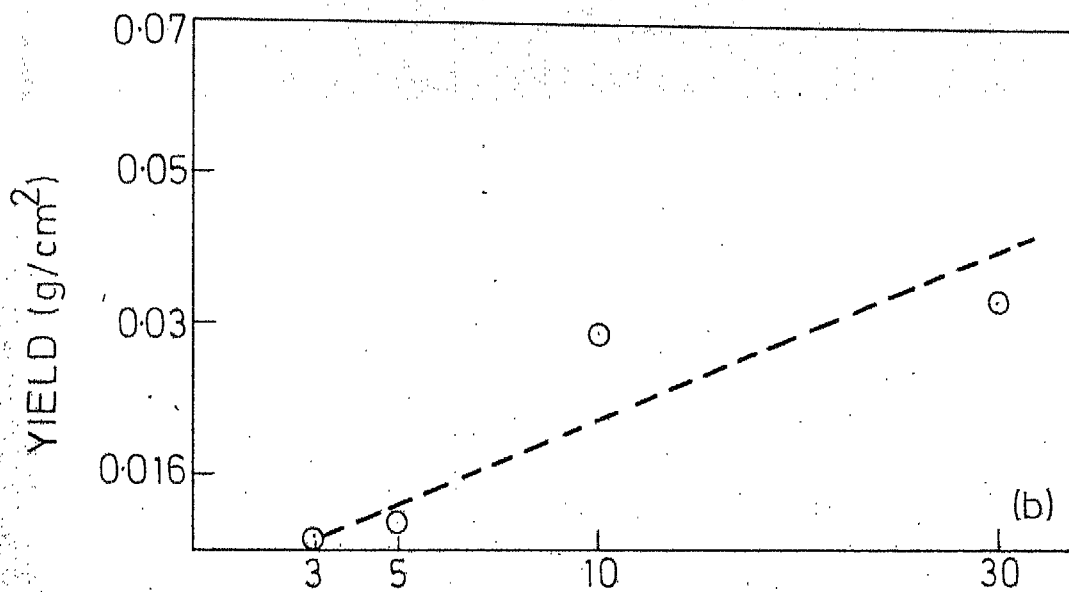
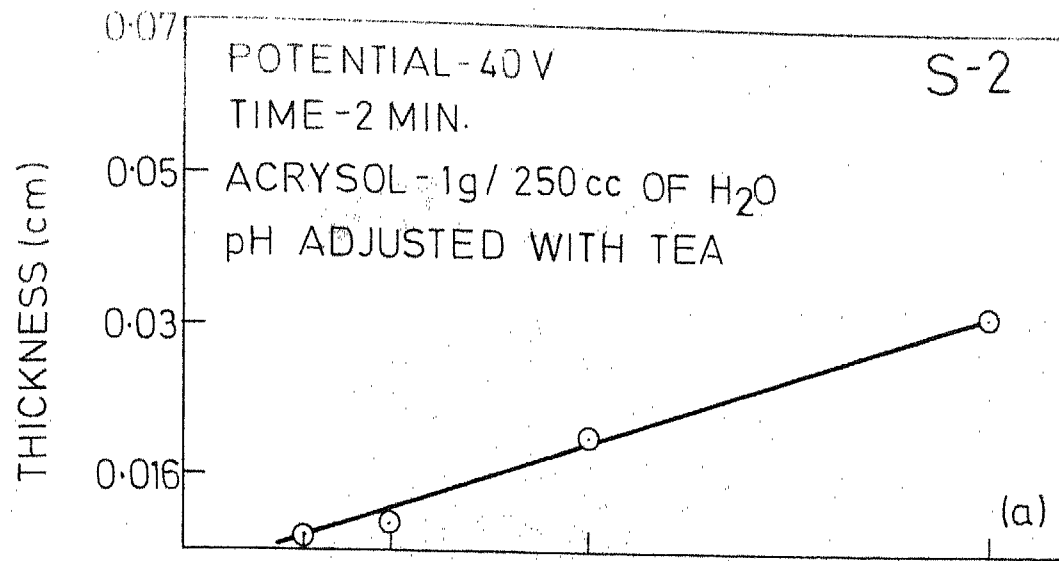


FIG.17 VARIATION OF THICKNESS, YIELD AND DENSITY WITH AMOUNT OF TiO₂

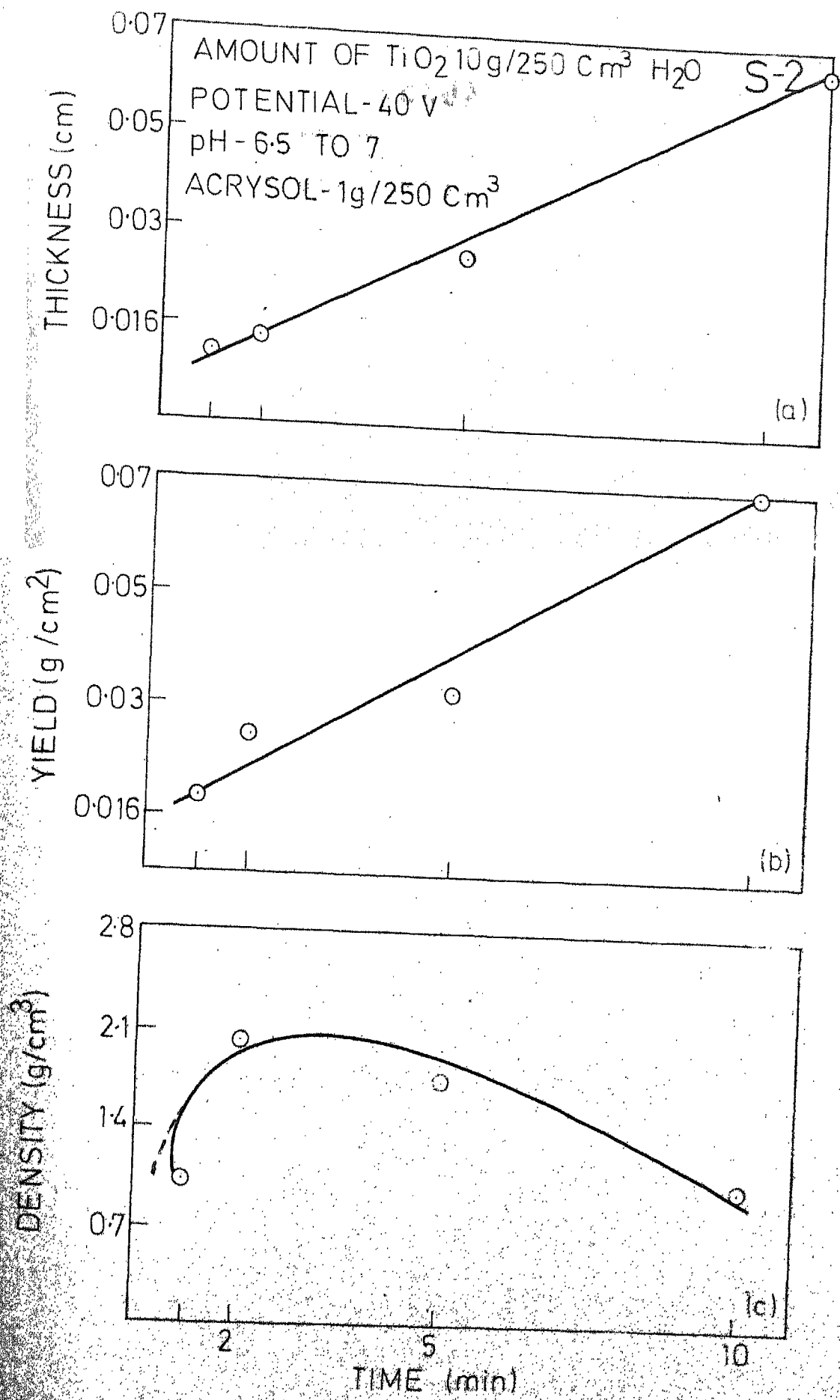


FIG.18 VARIATION OF THICKNESS, YIELD AND DENSITY WITH TIME

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